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POLAROGRAPHIC BEHAVIOR OF THENOYLTRIFLUOROACETONE  
(TTA) AND RELATED COMPOUNDS. ALKALINE CLEAVAGE OF  
TTA. COMPLEXATION OF TTA WITH BORATE. ANALYTICAL  
DETERMINATION OF TTA.

by

Philip J. Elving and Clarence M. Callahan

Technical Report No. 1

to the

OFFICE OF NAVAL RESEARCH

Under Project No. NR 051-310

Contract No. N6onr-23225

at the

University of Michigan

January 15, 1953

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Based on work done under

Project No. NR 055-211

and

Project No. NR 051-318

Contract No. N6onr-26915

Contract No. N6onr-23225

at

The Pennsylvania State College

at

University of Michigan

January 15, 1953

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## Introduction

The work described in this report had its origin in an attempt to develop a simple and reliable method for studying the kinetics of reactions involving thenoyltrifluoroacetone. When the desirability became apparent of investigating in greater detail the reduction mechanism and complexation of thenoyltrifluoroacetone, support for the work was shifted from the project supported by the Office of Naval Research on new analytical technics for studying reactions to one supported by the Atomic Energy Commission. This was done in view of the interest of the A.E.C. on the use of TTA in metal complexation.

This manuscript is also being submitted to the Chicago Operations Office of the A.E.C. as Report No. 2, COQ-119, on Contract No. AT(11-1)-70, Project No. 8.

This report will probably be submitted to the Journal of the American Chemical Society for publication.

Philip J. Elving

(CONTRIBUTION FROM THE PENNSYLVANIA STATE COLLEGE  
AND THE UNIVERSITY OF MICHIGAN)  
Polarographic Behavior of Thenoyltrifluoroacetone (TTA)  
and Related Compounds. Alkaline Cleavage of TTA.  
Complexation of TTA with Borate.  
Analytical Determination of TTA.  
Philip J. Elving and Clarence M. Callahan

ABSTRACT

Thenoyltrifluoroacetone (TTA) gives two polarographic waves in chloride, acetate and ammonia buffers, but only one wave in borate and phosphate buffers. The absence of one wave in the latter media is attributed to the complexation of TTA with buffer components. By correlating the half-wave potentials and behavior of TTA with those of thiophene, acetothienone, thenoylacetone, trifluoroacetylacetone and acetylacetone, each TTA wave is assigned to the reduction of a definite carbonyl group in the compound.

The polarographic evidence indicates the first wave to be due to a one-electron reduction of the carbonyl group adjacent to the trifluoromethyl group, followed by dimerization to form the pinacol. The second wave is due to the reduction of the thenoyl carbonyl group to the carbinol.

An analytical study showed that the diffusion current is a linear function of the concentration; optimum analytical results are secured in acetate buffer. The trends and anomalous effects in the polarographic behavior of TTA are discussed. The alkaline fission of TTA in ammonia buffer was followed polarographically; the data indicated a zero order reaction.

The nature of the interaction between boron species and the carbonyl group adjacent to the trifluoromethyl group is examined. The complex resulting is possibly due to the formation of a four-membered ring between boron and the two hydroxyl group oxygens on the carbon of the hydrated carbonyl group.

2-Thenoyltrifluoroacetone, first prepared by Reid and Calvin<sup>1</sup>

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(1) J. C. Reid and M. Calvin, J. Am. Chem. Soc., 72, 2948 (1950).  
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and usually referred to as TTA, forms complex molecules with various metal ions in suitable solutions. As the amount of complexing is pH-dependent, the separation of ordinarily very difficultly separable mixtures of ions is possible by properly adjusting the pH. The extraction of zirconium from hafnium through the use of TTA was considered to be one of the major achievements in chemistry for 1951.

The present investigation was undertaken to determine the general behavior of TTA at the dropping mercury electrode. In well buffered solution TTA presents a number of structures that should be amenable to electrolytic reduction such as the trihalogenated carbon atom alpha to a carbonyl group, the carbonyl group alpha to an unsaturated cyclic structure, the beta-diketone structure, and the conjugated double bond system, which through keto-enol tautomerism, should materially increase the number of electro-reducible structures in the molecule.

In order to identify the two waves generally given by TTA with the electrochemical reduction, of particular electro-reducible groups in TTA, the compound was considered to be a possible

derivative or composite of thiophene, acetothienone, thenoyl-acetone, trifluoroacetylacetone and acetylacetone. It was assumed that if one of the component units of a composite structure produces a polarographic wave when the component unit exists as a discrete molecule, the component unit will produce this or a related wave when it is a part of the composite structure with, of course, due consideration being given to the influence of the rest of the molecule.

By thus correlating the polarographic data of TTA with those of compounds which may be considered as component parts of its structure, it was possible to assign the presence of each TTA wave in a particular buffer to the electroreduction of a definite functional group in TTA, and to formulate reactions to account for the observed reductions. The polarographic constants of TTA in the different buffers were compared and trends noted; suitable explanations were postulated for the anomalous behavior observed in some buffer systems. The applicability of the polarograph for the detection and estimation of TTA was studied.

### Experimental

Chemicals. The TTA, used without further purification, was a research sample, kindly furnished by the Dow Chemical Company. Acetone, methyl ethyl ketone, acetylacetone and thiophene were redistilled prior to use. Acetothienone was furnished by Dr. Robert W. Taft. Trifluoroacetylacetone was redistilled from a sample prepared in this laboratory.

Buffer systems, prepared from analytical reagent grade chemicals, were used at the pH indicated: No. 1, 1.0 M KCl

with added HCl, 1.0; No. 2, 1.0 M sodium acetate with added acetic acid, 5.2; No. 3, 1.0 M ammonium chloride with added ammonium hydroxide, 8.2; No. 4, 0.05 M sodium tetraborate decahydrate, 0.90 M KCl and added NaOH, 9.2; No. 5, 0.22 M disodium hydrogen phosphate duodecahydrate with added NaOH, 12.0. The concentrations were such as to give an ionic strength level of 1.0 in the final test solution.

The nitrogen used for degassing was deoxygenated and equilibrated by bubbling successively through an alkaline pyrogallol solution, sulfuric acid, water and a portion of the test solution.

Apparatus. The polarographic curves were obtained with a calibrated Fisher Electrode, recording maximum galvanometer deflection. A Beckman model G pH meter was used. A piece of Corning marine barometer tubing provided a capillary with a  $\bar{m}$  value of 1.14 mm./sec. at open circuit in 0.1 M KCl solution. All  $E_{\frac{1}{2}}$  values are against the S.C.E. at 25.0° unless other temperatures are specified. The temperature of the saturated calomel electrode and the sample cell was kept constant by means of a constant temperature bath which supplied circulating water for the water-jacketed H-cell used<sup>2</sup>.

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(2) J. C. Komyathy, F. Malloy and P. J. Elving, Anal. Chem., 24, 431 (1952).  
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Procedure. Stock solutions were made by dissolving the requisite weight of the ketone in 25 ml. of ethanol and diluting with distilled water to volume in a 250-ml. volumetric flask. The test solution was prepared by pipetting 5.00 ml. of stock solution into a 50-ml. volumetric flask and diluting to the mark

with the desired buffer. The test solution was deoxygenated for 10 minutes and then electrolyzed at a constant head of mercury (67 cm.). The nitrogen atmosphere was maintained throughout the electrolysis.

#### Observed Behavior of TTA

Solvents for TTA. TTA is sparingly soluble in water. Initial investigation to find a suitable solvent for TTA revealed that acetone and methyl ethyl ketone were unsuitable, since, as subsequently discussed, they produce a well-defined wave in ammonia buffer, when their concentrations were decimolar or larger.

Ten per cent ethanol was found to be a suitable solvent for TTA. The requisite weight of TTA was first dissolved in a small quantity of 95% ethanol, and distilled water was then added, with shaking, to the desired volume. Millimolar quantities of TTA may also be dissolved without an organic solvent in distilled water by prolonged shaking at 50-60°C.

Thenoyltrifluoroacetone. Initial polarograms of aqueous solutions of TTA containing 1% ethanol in the various buffer systems are tabulated in Table I. In the chloride buffer at pH 1.0 two waves were detected. The first wave was small and poorly defined with the result that  $E_1$  could not be definitely located, but it occurred at approximately  $-0.78$  v. The second wave at  $-0.92$  v. was larger, but, unfortunately, merged with a pronounced maximum. Because of these limitations, no further work was done in this buffer system.

In acetate buffer at pH 5.2, two well defined waves are produced at  $-0.98$  and  $-1.17$  v. The  $i_d$  of the second wave is more than twice that of the first wave.



In the ammonia buffer at pH 8.2 two well defined waves are produced,  $E_{1/2}$  of -1.23 v. and -1.39 v. The  $i_d$  of the first wave is appreciably larger than that of the second wave, while in the same buffer at pH 9.2 the  $E_{1/2}$  shift to -1.32 and -1.45 v., and the  $i_d$  of the second wave is nearly twice as large as that of the first wave.

In borate buffer at pH 9.2, the first wave is absent;  $E_{1/2}$  of the second wave is -1.48 v. Phosphate buffer at pH 12.0 also give only one wave at -1.47 v. The  $i_d$  is considerably suppressed at this pH.

n-Values. Values of  $\underline{n}$  calculated from the Ilkovic equation are tabulated in Table II; the value of the diffusion coefficient of TTA used was calculated from the Stokes-Einstein equation as  $0.15 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$  (see Appendix I for calculation). In borate buffer  $\underline{n}$  is approximately 3; in ammonia buffer,  $\underline{n}$  is 3 for the first wave and 2 for the second wave; in acetate buffer,  $\underline{n}$  is 1 for the first wave and 2 for the second wave.

A more exact determination of  $\underline{n}$  was attempted by coulometric measurement<sup>3</sup>. A number of one and two millimolar solutions of

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(3) J. J. Lingane, J. Am. Chem. Soc., 67, 1916 (1945).  
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TTA were electrolyzed at -1.40 v. in acetate buffer at pH 5.0; at this potential both reduction processes occur and  $\underline{n}$  was found to be approximately 4. Polarograms of the reduced product showed that the first wave had disappeared, and that only a greatly diminished second wave remained. A check of the pH of the buffered solutions after electrolysis showed that it had remained constant.

Values of  $n$  calculated from the slope of the polarographic wave are approximately one in all buffers and at all concentrations.

Current-Controlling Process. The temperature coefficient for the current of the first wave indicates a kinetic-controlled process which is very well explained by subsequent equation (7). The current behavior of the second wave indicates diffusion-control. In general,  $E_{1/2}$  of the second wave shifts to a slightly more positive value and  $E_{1/2}$  of the first wave to a slightly more negative value (Table III).

Variation of  $i_d$  with drop-time, i.e., head of mercury, (Table IV) also shows the first wave to be due to a kinetic-controlled process. The second wave appears to be diffusion-controlled in borate and acetate buffers, but an adsorption process is indicated in ammonia buffer.

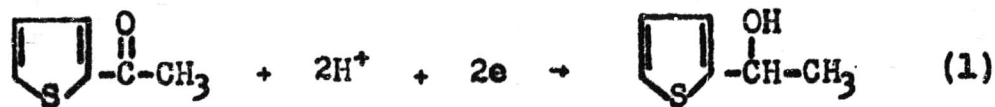
pH Dependence of the Ketones. Both waves of TTA shift to more negative  $E_{1/2}$  values with increase of pH (Fig. 1). In pH greater than 9.0,  $E_{1/2}$  values become constant. The waves of acetothienone, thenylacetone and trifluoroacetylacetone also show this pH-dependence, indicating similar reduction mechanisms to those of TTA.

#### Behavior of Compounds Related to TTA

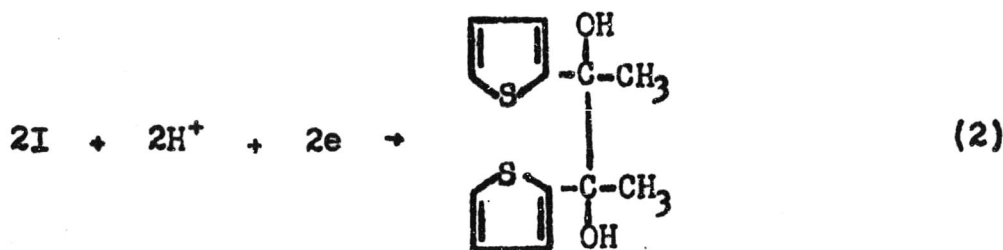
Thiophene. Since thiophene produced no wave in any of the buffer systems or in unbuffered 0.1 M lithium chloride, it may be concluded that the thiophene ring is not reducible under the experimental conditions used and that the thiophene radical is not reduced in TTA.



Acetothienone. Acetothienone (I), which differs from thiophene by possessing a reducible carbonyl group conjugated to the ring, produces one wave in each of the buffer systems. Hence it may be assumed that the wave is produced by the reduction of the carbonyl group alpha to the thiophene ring, probably by one of the following reactions:



I



II

The latter (equation 2) is lent some credence by the preparative electrolytic reduction of ketones<sup>4</sup> in which pinacols are

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(4) D. H. Hey and W. A. Waters, Chem. Revs., 21, 169 (1937).  
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produced. A free radical mechanism most simply explains this reaction:



This hypothesis receives further confirmation from the fact that the electrolytic reduction of acetone at a mercury cathode produces mercury diisopropyl<sup>5</sup> and at a lead cathode lead tetraalkyl.

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(5) C. J. Haggerty, Trans. Am. Electrochem. Soc., 56, 421 (1927).  
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Since the  $E_{\frac{1}{2}}$  values of TTA and acetothienone show a correspondence between the second wave produced by TTA and the only wave of acetothienone, the more negative TTA wave is probably identical with the acetothienone wave and can be identified with the reduction of the carbonyl alpha to the thiophene ring.

Thenoylacetone. Thenoylacetone differs from TTA in that hydrogens have replaced the three fluorine atoms of TTA. In ammonia buffer, thenoylacetone has two waves; the second  $E_{\frac{1}{2}}$  compares with the corresponding  $E_{\frac{1}{2}}$  of TTA, which has been assigned to the reduction of the carbonyl alpha to the thiophene ring. In thenoylacetone the only other reducible group is the carbonyl gamma to the thiophene ring. Therefore, the first wave of thenoylacetone is probably due to the gamma carbonyl reduction, and, by analogy, the first wave of TTA is caused by reduction of the same group. In acetate buffer thenoylacetone differs from TTA in lacking the first wave. In borate buffer thenoylacetone again differs from TTA by producing two waves against one for TTA. These two deviations from the expected effect, which indicate that the trifluoro group has a marked effect on the properties of TTA, will be subsequently discussed. All the  $E_{\frac{1}{2}}$  values of thenoylacetone agree quite well with those of TTA.

Trifluoroacetylacetone. This compound produces one wave in acetate and ammonia buffers, whose  $E_{\frac{1}{2}}$  values compare closely with those of the second wave of TTA.

Acetylacetone, Acetone, Methyl Ethyl Ketone. Acetylacetone gives one wave in ammonia buffer and no waves in the other buffer systems. This behavior is quite similar to that of acetone and methyl ethyl ketone and may be ascribed to the reduction of the

imino group formed from the ketone and free ammonia. This wave appears to be unique to ammonia buffers; Zuman<sup>6</sup> has reported

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(6) P. Zuman, Nature, 165, 485 (1950).  
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a wave for acetone at -1.6 v. in ammonium sulphate-ammonia buffer at pH 9.3, which he attributed to the reduction of the imino group of the ketimine in equilibrium with the acetone and ammonia:



Zuman concluded that the wave height was influenced by the concentration of the free ammonia available and is a linear function of the acetone concentration. He claimed that he found well defined waves in millimolar acetone solutions, and pointed out the danger of volatilizing the acetone out of the solution while degassing. In the present work, in ammonium chloride-ammonia buffer of pH 8.2, acetone gave a well defined wave at -1.44 v. and methyl ethyl ketone a similar wave at -1.43 v. (Table I). The discrepancy with the  $E_1$  of acetone reported by Zuman may be attributed to differences<sup>2</sup> in the pH and ionic strength of the buffers used<sup>7</sup>. The difficulty of detecting small

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(7) P. J. Elving, J. C. Komyathy, R. E. Van Atta, Ching-Sing Tang, and I. Rosenthal, Anal. Chem., 23, 1219 (1951).  
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concentrations of acetone and methyl ethyl ketone in the present case is believed to be due to the fact that the equilibrium of equation (4) is far to the left.

From the close correlation of the half-wave potentials for TTA and related compounds (Table V), it is evident that the first TTA wave is due to the reduction of the carbonyl group in the trifluoroacetyl portion of TTA, and the second wave to the reduction of the carbonyl group in the thenoyl portion.

In order to assign mechanisms for the electrode reactions, it is necessary to consider the various species of TTA present in aqueous solution. Zebroski<sup>8</sup> concluded from spectral studies

(8) E. Zebroski, Atomic Energy Commission, BC-63 (1947); Ph.D. Thesis, University of California.

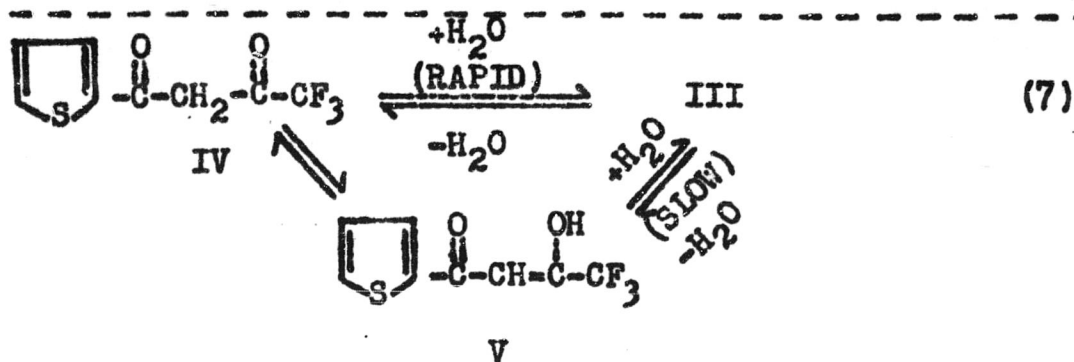
of the aqueous TTA solution that the compound exists primarily as the hydrate:



Reid and Calvin<sup>1</sup> showed that only 1.6% of TTA in aqueous solution is present in the enol form, but that 94.5% of TTA in dry benzene solution is present in the enol form. Stabilization of the hydrate is due both to the strong inductive effect of the adjacent fluorine atoms, which is conducive to the production of a positive carbon capable of adding a hydroxyl ion, and to possible formation of a strong hydrogen bond between the oxygen and fluorine on adjacent carbon atoms. This push-pull effect would explain

the stabilization of similar hydrates such as those of chloral, glyoxal, glyoxylic acid, etc. An equilibrium is indicated,<sup>9</sup>

(9) H. M. Irving, Quart. Revs., 5, 200 (1951).



in which the hydrated form, III, is the principal species present. On the other hand, since hydration is not possible in dry benzene, the enol is the principal species present, which is stabilized by hydrogen bonding either of the O-H-O or O-H-F type, or possibly both. Obviously, since hydration represses enolization and the hydrated form presents only one reducible carbonyl, the presence of two waves in acidic and ammonia buffers must be due (1) to the reduction of the carbonyl group alpha to the thiophene ring and (2) to the reduction of the small amount of the keto-enol species of the gamma carbonyl that remains unhydrated and is produced during the life-time of the mercury drop (equation 7).

Since an acidic environment favors the keto modification and an alkaline medium the enolic, the small  $i_d$  of the first wave in acid media is due to the acidic repression of the enolic species as well as to the excessive hydration of TTA. The shift to the enolic form in alkaline buffer accounts for the increased  $i_d$  of the first TTA wave in ammonia buffer of pH 8.2.

Between pH 8.2 and 9.2 in ammonia buffer,  $i_d$  of the first wave passes through a maximum (Fig. 2), due to competition between the increases in the rates of enol formation and of alkaline cleavage of the hydrated TTA to acetothienone and trifluoroacetate<sup>10,11</sup>:



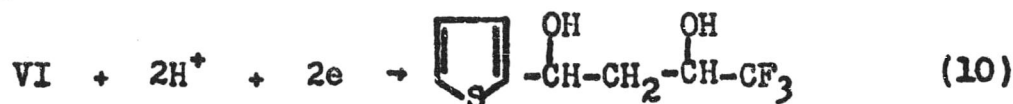
(10) E. H. Cook and R. W. Taft, J. Am. Chem. Soc., **74**, 6103 (1952).

(11) L. Wish and R. A. Bolomey, J. Am. Chem. Soc., **72**, 4486 (1950).

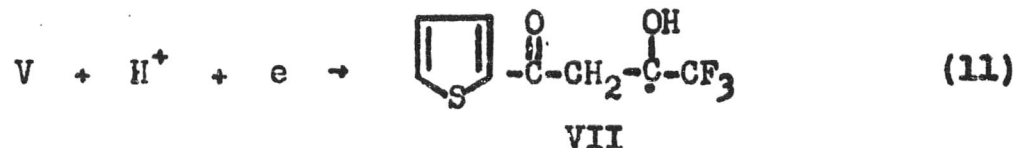
On the basis of a two-electron reduction for each wave, the first wave could be considered to involve the reduction of the enol:



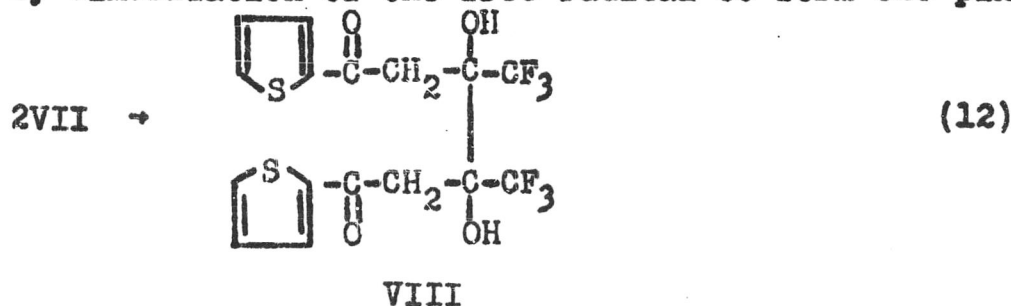
The second wave would be due to the two-electron reduction of the alpha carbonyl:



On the other hand, if the n-values calculated from the Ilkovic equation are accepted, the first wave in the acetate buffer might be a one-electron reduction of the enolic form,

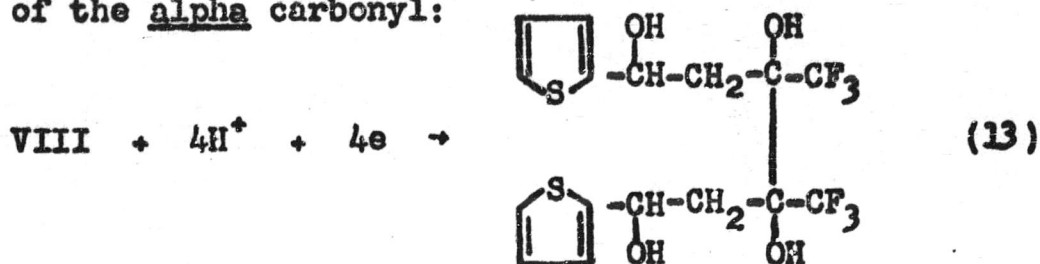


followed by dimerization of the free radical to form the pinacol:





The  $n$  value of one for the first wave calculated from the slope of the polarographic wave tends to substantiate the free radical mechanism. The second wave would then involve the two-electron reduction of the alpha carbonyl:



An  $n$  value of one for the slope of the second wave indicates that the two-electron reduction of the carbonyl group proceeds stepwise; one electron is added in a slow potential-determining process and the other by a fast process.

Unfortunately, it is not possible at present to determine which of the two over-all processes is the path followed, but the polarographic evidence strongly favors the pinacol process.

#### Alkaline Cleavage of TTA

In alkaline buffers, the magnitude of  $i_d$  of TTA depends on the length of time the stock solution of TTA has been mixed with the buffer. Such variation is not observed in acidic buffer. The aqueous stock solutions themselves were quite stable for several months. Table VI gives the data for a time- $i_d$  study of TTA in ammonia buffer at 25°C. The first wave eventually disappears, while the second wave passes through a maximum. Initially, the diminution of the first wave follows a zero-order reaction rate given by the equation,  $k = x/t$ . The straight-line first portion of the  $i_d$ -time curve, when extrapolated to zero time, gave a value of 4.65 microamperes. The zero-order disappearance of the first wave was operative until  $i_d$  had been reduced to 45% of its initial value. The shift of  $E_{1/2}$  for both waves to more positive values by 0.01 v. as the reaction proceeds, is probably

due to the effect of concentration on  $E_1$  as subsequently discussed. The alkaline cleavage is sensitive, i.e.,<sup>12</sup> accelerated, to light.

The gradual disappearance of the first TTA wave in the ammonia buffer is probably due to rapid conversion to the enolate modification (equation 7). The alkaline environment shifts the equilibrium in the direction of the enolate, and the hydrated form of TTA becomes the minor species present in the solution. The hydrated TTA form is cleaved in the alkaline buffer as described by Pearson and Mayerle<sup>12</sup>. The slow step is probably the back-

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(12) R. G. Pearson and E. A. Mayerle, J. Am. Chem. Soc., 73, 926 (1951).

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hydrolysis of the enolate to the hydrated form. The latter is then cleaved as fast as it is formed.

#### Complexation of TTA with Borate

The absence of the first TTA wave in borate and phosphate buffers is apparently due to the complexing of the borate or phosphate with the ketone through the hydroxyl groups of the hydrated species. This complexation may best be understood by considering the species present in aqueous borate-TTA mixture. Borax dissociates in solution into boric acid and sodium metaborate; the addition of sodium hydroxide has been shown to convert boric acid to sodium metaborate. Thus the buffer effectively consists of boric acid, sodium metaborate and sodium tetraborate<sup>13</sup>. Tsuzuki<sup>14</sup> who studied the nature of complex

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(13) J. H. Hibben, Am. J. Sci., 35-A, 113 (1936).

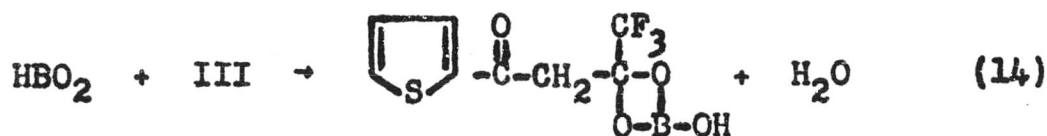
(14) Y. Tsuzuki, Bull. Chem. Soc. Japan, 16, 23 (1941); ibid., 13, 337 (1938); Y. Tsuzuki and Y. Kemura, ibid., 15, 27 (1940).



formation between boric acid and organic polyoxy compounds, found that boric acid has very feeble ability for complex formation with non-ionizable polyoxy compounds, while alkali borate shows strong complexing activity. The order of activity is  $\text{H}_3\text{BO}_3 \ll \text{Na}_2\text{B}_4\text{O}_7 < \text{KBO}_2$ . Strong complexes were formed between borate and polyhydric alcohols. This property has long been used when mannitol or glycerol is added in boric acid titration. Since Raman spectra<sup>15</sup> indicate that the metaborate ion is

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(15) J. R. Nielson and H. E. Ward, J. Chem. Phys., 5, 201 (1937).

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linear,  $\text{-O-B-O-}$ , or slightly bent<sup>13</sup>, it is quite possible that on mixing the metaborate ions present in the alkaline tetraborate buffer immediately form a strong complex with the hydrated TTA.



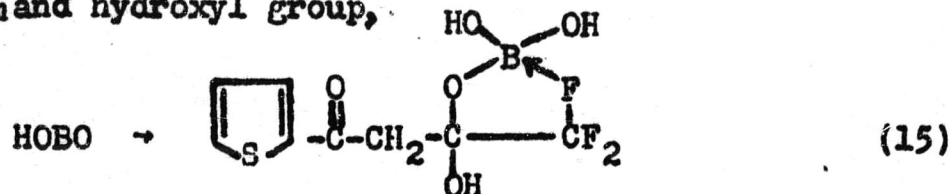
The work of Reppere and La Mer<sup>16</sup> strongly indicates com-

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(16) R. E. Reppere and V. K. La Mer, J. Phys. Chem., 47, 204 (1943).

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plexation of this type between borate or metaborate and polyhydroxy alcohols with at least two adjacent carbon atoms containing alcoholic groups. The formation of orthoboric or metaboric esters for this type of alcohol was excluded.

The question of the stability of a four-membered ring as postulated in equation 14 naturally arises. Since the ring is quite heterocyclic, its formation is not improbable, but may be unusual.

Another possible boron complex would involve adjacent fluorine atom and hydroxyl group,



The remaining hydroxyl group could then be complexed in the same fashion.

The presence of both waves of thenoylacetone in borate buffer would tend to eliminate the possibility of boron complexing with the beta-diketone grouping, since the waves would be expected to be suppressed if complexation occurred. This type of complexation appears unlikely also in TTA as the second wave is entirely normal in all respects. A complex that included the thenoyl group should at least materially reduce the size of the second TTA wave; this does not occur.

The presence of the first wave of thenoylacetone in borate buffer now becomes clear. Since there are no adjacent halogens to stabilize the hydrated form of the ketone, the necessary hydroxy groups are not present to form a strong complex with the borate buffer. Consequently the carbonyl group is reduced and the first wave is present.

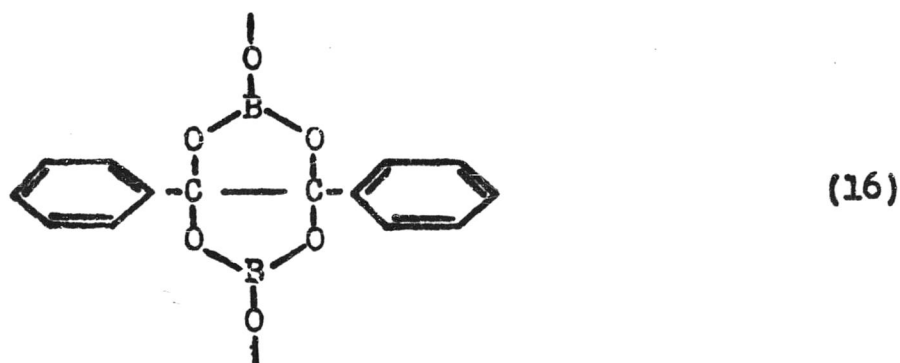
The absence of the first wave of thenoylacetone in acetate buffer is not immediately obvious from the data; possibly hydrogen bonding of the enol is involved. The absence of a strong electron-withdrawing group adjacent to the gamma carbonyl gives normal ketone behavior in this case.

Pasternak<sup>17</sup> followed polarographically the rate of complexa-

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(17) R. Pasternak, Helv. Chim. Acta, 30, 1984 (1947).

tion of boric acid with benzil. In acid solution little or no reaction was detected. On increasing the alkalinity, the polarographic wave was reduced in height to a constant limiting value. On acidification, the wave increased to its original level, showing that the complex formation is reversible. Pasternak also proved the existence of the complex spectrophotometrically. The complex, which contained one molecule of benzil united to two of boric acid, was given as



Apparently, a much stronger complex is formed in borate buffer with TTA than with benzil, since the first TTA wave is completely absent, while the benzil wave is only reduced in size.

#### Polarographic Determination of TTA

From the data given in Table II for TTA in the concentration range of 0.2 to 1.2 millimolar in the various buffers in 1% ethanol, it is possible to determine the accuracy of the polarographic method for the determination of TTA in dilute solution.

Half-wave Potentials.  $E_{\frac{1}{2}}$  for the two TTA waves are less than 0.2 v. apart, which materially affects the accuracy of determining  $E_{\frac{1}{2}}$  and  $i_d$  for the individual waves. There is an apparent slight shift of  $E_{\frac{1}{2}}$  with variation of concentration from 0.2 to 1.2 mM, which is 0.01 v. for the borate buffered

solution, and 0.01 v. for the first wave and -0.01 v. for the second wave in ammonia buffer; there is no observable shift in acetate buffer. The effect is probably due to the small separation of the waves, since the effect increases with concentration and the waves tend to merge with increasing concentration, making the task of separating the two waves more difficult.

Diffusion Currents. The value of  $i_d/c$  for the first wave increases with increasing pH until between 8.2 and 9.2 it passes through a maximum (Fig. 2). This relation reflects the increase of the enol concentration with increase of pH until between 8.2 and 9.2 the alkaline cleavage of TTA becomes appreciable and acts in opposition to the enol formation. Since the second wave also passes through a maximum beyond pH 9.2, the cleavage of TTA evidently also affects this wave.

The sum of  $i_d$  for the two waves as well as for the individual waves vs. concentration in different buffers are plotted in Fig. 3. In tetraborate buffer a slight deviation of  $i_d$  from linearity is noticeable at high concentration. In general, the relations in ammonia and acetate buffers are linear up to 1.2 mM, the largest concentration measured; obviously, the sum of the two waves gives the best result. Diffusion current constant values are summarized in Table VII.

For the quantitative analysis of dilute solutions of TTA, either an acetate or an ammonia buffer produces reproducible results; the ammonia buffer produces the larger  $i_d$  and hence minimizes the relative error. The chief disadvantage of this buffer lies in the fact that TTA cleaves in alkaline media. This, however, can be minimized by not mixing the stock sample solution of the TTA with the buffer until immediately before

electrolysis of the sample, and by making the pH of the buffer as nearly neutral as is consistent with good buffering practice, i.e., 8.2. Although  $i_d$  values in acetate buffer are small, using ordinary techniques, the values are easily reproducible to within 2 or 3% of the mean value.

Analysis of Non-alcoholic Solutions. Table VIII contains the data for solutions in acetate buffer at pH 5.0, which contained no alcohol. The mean deflection of the galvanometer was recorded instead of the usual maximum. In general, the results are less consistent than those in 1% alcohol solution (Table II), probably due either to the mean galvanometer deflection not giving as reliable results as the maximum, or to the absence of ethanol in the stock solution.

Acknowledgment. The authors wish to thank the Atomic Energy Commission which supported the research project upon which this work was done.

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# APPENDIX I

## Calculation of $\underline{n}$ Values

Three  $\underline{n}$  values were calculated; one was based on the Ilkovic equation,

$$i_d = 605 \underline{n} D^{\frac{1}{2}} C m^{2/3} t^{1/6} \quad (17)$$

one was based on coulometric measurements, and the third was based on the following relation as derived from the equation for the wave,

$$E_{\frac{1}{4}} - E_{3/4} = 0.0563/\underline{n} \text{ at } 25^\circ\text{C.} \quad (18)$$

The value of  $\underline{n}$  in the Ilkovic equation for the average current represents the number of electrons involved in the reduction of one molecule of the electroactive substance which results in current flow;  $i_d$  is the diffusion current in micro-amperes at any given time  $t$  (in seconds) during the life of the drop.  $D$  is the diffusion coefficient of the electroactive material ( $\text{cm.}^2 \text{ sec.}^{-1}$ ),  $C$  is the concentration of the electroactive substance in millimoles per liter and  $\underline{m}$  is the weight of mercury flowing from the capillary per second in  $\text{mg. sec.}^{-1}$ ; 605 is a constant involving the geometry of the mercury drop, the value of the Faraday, etc.

All the data necessary to calculate  $\underline{n}$  from the Ilkovic equation are usually available except the diffusion coefficient. This value may be approximated by using the Stokes-Einstein diffusion equation:

$$D = (RT/N) [(4Nd)^{1/3} / 6\eta(3M)^{1/3}] \quad (19)$$

where  $N = 6.03 \times 10^{23}$ ,  $R = 8.315 \times 10^7 \text{ ergs deg}^{-1}$ ,  $\eta$  = viscosity coefficient of the solvent,  $M$  = molecular weight of the substance,  $d$  = density of the substance, and  $T = 298^\circ\text{K}$ . Combining these values into a single term, we have

$$D = 2.96 \times 10^{-7} / m(V_{\dots})^{1/3} \text{ cm.}^2 \text{ sec.}^{-1} \text{ at } 25^\circ\text{C.} \quad (20)$$



Here  $V_m$  is the approximate volume of the substance in the pure solid state (mol. wt./density). The viscosity coefficient ( $\eta$ ) of pure water at 25°C. is  $8.93 \times 10^{-3}$  dyne<sup>-1</sup> sec.<sup>-1</sup> cm.<sup>-2</sup>, and hence at infinite dilution in aqueous solution at 25°C.

$$D_0 = 3.32 \times 10^{-5} / (V_m)^{1/3} \text{ cm.}^2 \text{ sec.}^{-1} \quad (21)$$

Obviously, such a diffusion coefficient value is not valid in highly buffered solutions. However, since it is necessary only to distinguish between small integral values of  $\underline{n}$  when inserted in the Ilkovic equation, the results are usually sufficiently accurate.  $D$  for TTA is calculated to be  $0.62 \times 10^{-5}$  cm.<sup>2</sup> sec.<sup>-1</sup>

Tomes<sup>18</sup> suggested using the  $\underline{n}$ -value from equation (18) as

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(18) J. Tomes, Collection Czechoslov. Chem. Commun., 2, 12 (1937).

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a criterion of reversibility. Thus an  $\underline{n}$ -value less than one usually indicates that the electrode is irreversible. This equation is derived from the fundamental Heyrovsky-Ilkovic equation<sup>19</sup> for the polarographic wave at 25°:

$$E_{d.e.} = E_{\frac{1}{2}} - (0.0591/\underline{n}) \log [1/(i_d - i)] \quad (22)$$

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(19) J. Heyrovsky and D. Ilkovic, Collection Czechoslov. Chem. Commun., 7, 198 (1935).

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where  $i$  is the current in microamperes at the corresponding potential  $E_{d.e.}$  in volts,  $i_d$  is the diffusion current in microamperes, and  $E_{\frac{1}{2}}$  is the half-wave potential. Then  $E_{3/4}$  and  $E_{\frac{1}{4}}$  are the potentials at the points where  $i_{3/4} = (0.75) i_d$  and  $i_{1/4} = (0.25) i_d$ . The  $\underline{n}$ -values thus calculated for TTA are approximately equal to one in all buffers and at all concentrations.

TABLE I

POLAROGRAPHIC CHARACTERISTICS OF TTA AND RELATED COMPOUNDS AT 25° C.

Compound	Buffer No.	pH	Concn. mM	WAVE I			WAVE II		
				$E_{1/2}$ v.	$i_d$ ua.	$i_d/c$	$E_{1/2}$ v.	$i_d$ ua.	$i_d/c$
Thenoyltrifluoroacetone	1	1.0	0.4	0.775	0.26	0.65	0.926	2.18	5.45
	1	1.0	0.4	0.789	0.23	0.58	0.920	1.95	4.88
	2	5.2	0.5	0.976	0.75	1.50	1.173	1.94	3.89
	2	5.2	0.5	0.977	0.75	1.50	1.173	1.89	3.78
	3	8.2	0.5	1.232	3.02	6.03	1.392	2.08	4.16
	3	8.2	0.5	1.236	3.07	6.14	1.396	2.08	4.16
	3	9.2	0.8	1.322	2.65	3.31	1.452	4.99	6.24
	4	9.2	0.5	No wave			1.480	3.56	7.12
	4	9.2	0.5	No wave			1.479	3.59	7.18
	5	12.0	0.5	No wave			1.473	1.66	3.32
Thiophene	1 to 4	1 to 10	0.5	No wave			No wave		
Acetothienone	1	1.0	0.5	No wave			0.963	2.01	4.03
	2	5.1	0.5	No wave			1.255	1.82	3.64
	2	5.1	0.5	No wave			1.250	1.72	3.44



Acetothienone	3	8.2	0.5	No wave		1.407	3.54	7.08
	3	8.2	0.5	No wave		1.411	3.59	7.18
	4	10.0	0.5	No wave		1.493	2.78	5.57
	4	10.0	0.5	No wave		1.491	2.76	5.52
Thenoylacetone	2	5.0	0.639	No wave		1.152	3.05	4.77
	3	8.2	0.693	1.253	3.21	5.03	1.19	1.87
	4	9.2	0.639	1.346	1.26	1.97	1.69	2.64
	4	9.2	0.693	1.355	1.19	1.87	2.04	3.20
Trifluoroacetylacetone	1	1.0	1.065	No wave		No wave		
	2	5.0	1.065	No wave		1.216	1.10	1.04
	3	8.2	1.065	No wave		1.428	1.75	1.65
	4	9.2	1.065	No wave		No wave		
Acetylacetone	1, 2, 4			No wave		No wave		
	3	8.2	380.0	No wave		1.212	3.48	0.009
Acetone	1, 2, 4			No wave		No wave		
	2							
Methyl Ethyl Ketone	3	8.2	1370.0	No wave		1.437	7.75	0.006
	4							
	3	8.2	1100.0	No wave		1.429	2.96	0.003

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EFFECT OF pH AND BUFFER ON THE POLAROGRAPHIC CONSTANTS OF THENOLYTRIFLUOROACETONE  
AT VARIOUS CONCENTRATIONS IN 1% ETHANOL-WATER SOLUTION AT 25° C.

			WAVE I					WAVE II						
Buffer No.	pH	TTA Concn. mM	$E_1^0$ v.	$i_d$ ua.	$i_d/c$ ua./mM	ic	na	$n_b$	$E_1^0$ v.	$i_d$ ua.	$i_d/c$ ua./mM	ic	na	$n_b$
4	9.2	0.2	No wave						1.474	1.43	7.15	5.11	2.9	1.0
			No wave						1.479	1.46	7.31	5.22	3.0	1.0
			No wave						1.477	1.46	7.31	5.22	3.0	0.9
			No wave						1.478	1.44	7.18	5.17	3.0	0.9
			No wave						1.480	1.49	7.43	5.36	3.0	0.9
			No wave						1.477	1.45	7.25	5.22	3.0	0.9
			No wave						1.475	1.44	7.18	5.17	3.0	1.0
			MEAN											
			1.477	1.45	7.26	5.21	3.0	1.0						
4	9.2	0.5	No wave						1.480	3.56	7.13	5.14	2.9	0.8
			No wave						1.479	3.59	7.18	5.18	3.0	0.8
			No wave						1.471	3.54	7.07	5.08	2.9	0.8
			No wave						1.471	3.61	7.22	5.16	2.9	0.8
			No wave						1.470	3.59	7.18	5.17	3.0	0.8
			No wave						1.470	3.54	7.07	5.09	2.9	0.8
			No wave						1.474	3.57	7.14	5.14	2.9	0.8
			MEAN											

4	9.2	0.8	No wave	1.468	5.72	7.15	5.15	2.9	0.8
			No wave	1.470	5.69	7.12	5.13	2.9	0.7
			No wave	1.470	5.72	7.15	5.15	2.9	0.8
			No wave	1.470	5.72	7.15	5.18	3.0	0.8
			MEAN	1.470	5.71	7.14	5.15	2.9	0.8
4	9.2	1.2	No wave	1.469	7.82	6.52	4.70	2.7	0.7
			No wave	1.469	8.12	6.77	4.83	2.8	0.7
			No wave	1.467	7.65	6.37	4.59	2.7	0.7
			No wave	1.467	7.72	6.43	4.59	2.7	0.7
			No wave	1.464	7.70	6.42	4.62	2.7	0.7
			No wave	1.465	7.83	6.53	4.70	2.7	0.7
			No wave	1.462	7.64	6.37	4.58	2.7	0.7
			MEAN	1.466	7.78	6.49	4.66	2.7	0.7
3	8.2	0.2	1.234	1.385	0.88	4.42	3.16	1.8	0.9
			1.239	1.389	0.86	4.29	3.07	1.8	0.9
			1.238	1.389	0.88	4.42	3.16	1.8	0.8
			1.240	1.380	0.83	4.16	2.97	1.7	0.9
			1.239	1.385	0.84	4.19	3.01	1.7	0.9
			1.241	1.385	0.83	4.13	2.95	1.7	0.9
			1.236	1.388	0.86	4.32	3.09	1.8	1.0
			1.236	1.389	0.75	3.75	2.68	1.5	0.9
			MEAN	1.238	0.84	4.21	3.01	1.7	0.9

3	8.2	0.5	1.232	3.02	6.04	4.28	2.5	0.9	1.392	2.08	4.16	2.99	1.7	0.8
			1.236	3.07	6.14	4.35	2.5	1.0	1.396	2.08	4.16	2.99	1.7	0.8
			1.239	2.99	5.98	4.24	2.4	1.0	1.395	2.08	4.16	3.00	1.7	0.8
			1.233	3.04	6.08	4.28	2.5	1.0	1.397	2.08	4.16	2.97	1.7	0.8
			1.237	2.99	5.98	4.24	2.4	0.9	1.400	2.13	4.27	3.07	1.8	0.8
		MEAN	1.235	3.02	6.04	4.28	2.5	1.0	1.396	2.09	4.18	3.00	1.7	0.8
3	8.2	0.8	1.232	4.60	5.75	4.08	2.3	1.0	1.396	3.38	4.23	3.05	1.7	0.8
			1.230	4.86	6.08	4.28	2.5	1.0	1.398	3.51	4.39	3.14	1.8	0.8
			1.231	4.76	5.95	4.22	2.4	1.1	1.400	3.56	4.45	3.20	1.8	0.8
			1.231	4.68	5.85	4.15	2.4	1.0	1.401	3.35	4.19	3.02	1.7	0.8
			1.229	4.99	6.24	4.42	2.5	1.0	1.403	3.54	4.42	3.18	1.8	0.7
			1.233	4.65	5.82	4.12	2.4	1.1	1.400	3.51	4.39	3.16	1.8	0.7
			1.231	4.68	5.85	4.15	2.4	1.1	1.400	3.56	4.45	3.20	1.8	0.7
		MEAN	1.231	4.75	5.93	4.20	2.4	1.0	1.400	3.49	4.36	3.14	1.8	0.8
3	8.2	1.2	1.228	7.00	5.83	4.13	2.4	1.3	1.406	5.20	4.34	2.38	1.4	0.9
			1.227	6.88	5.74	4.04	2.3	1.0	1.404	5.00	4.16	2.97	1.7	0.8
			1.225	6.99	5.82	4.09	2.3	1.0	1.412	5.05	4.21	3.00	1.7	0.7
			1.224	6.94	5.78	4.06	2.3	1.1	1.404	5.10	4.25	3.03	1.7	0.9
			1.229	6.94	5.78	4.06	2.3	1.1	1.409	5.20	4.33	3.10	1.8	0.8
			1.226	7.08	5.91	4.15	2.4	1.0	1.407	4.90	4.08	2.92	1.7	0.8
		MEAN	1.227	6.97	5.81	4.09	2.3	1.1	1.407	5.08	4.23	2.90	1.7	0.8

2	5.17	0.2	0.987	0.32	1.59	1.10	0.6	0.8	1.174	0.78	3.87	2.70	1.5	1.3
			0.988	0.29	1.46	1.01	0.6	1.3	1.172	0.78	3.87	2.70	1.5	1.2
			0.971	0.29	1.46	1.01	0.6	1.2	1.170	0.80	4.00	2.82	1.6	1.1
			0.976	0.29	1.46	1.01	0.6	1.4	1.170	0.79	3.93	2.77	1.6	1.2
			0.978	0.32	1.59	1.10	0.6	1.2	1.175	0.77	3.87	2.70	1.5	1.4
		MEAN	0.980	0.30	1.51	1.04	0.6	1.2	1.172	0.78	3.91	2.74	1.5	1.2
2	5.17	0.5	0.976	0.75	1.50	1.04	0.6	1.1	1.173	1.94	3.89	2.71	1.5	1.0
			0.977	0.75	1.50	1.05	0.6	1.2	1.173	1.89	3.78	2.62	1.5	1.1
			0.975	0.79	1.58	1.09	0.6	1.0	1.172	1.91	3.82	2.69	1.5	1.1
			0.978	0.74	1.47	1.02	0.6	1.2	1.175	1.89	3.79	2.67	1.5	1.0
			0.983	0.79	1.58	1.10	0.6	1.0	1.177	2.01	4.04	2.84	1.6	1.1
		MEAN	0.978	0.76	1.53	1.06	0.6	1.1	1.174	1.93	3.86	2.71	1.5	1.1
2	5.17	0.8	0.976	1.17	1.46	1.02	0.6	1.3	1.172	3.07	3.84	2.70	1.5	1.0
			0.983	1.17	1.46	1.02	0.6	1.3	1.172	3.09	3.87	2.72	1.5	1.1
			0.984	1.12	1.40	0.98	0.6	1.8	1.174	3.22	4.03	2.84	1.6	1.0
			0.982	1.09	1.37	0.96	0.5	1.4	1.174	3.22	4.03	2.84	1.6	1.1
			0.980	1.17	1.46	1.01	0.6	1.4	1.172	3.17	3.97	2.79	1.6	1.1
		MEAN	0.981	1.14	1.43	1.00	0.6	1.4	1.173	3.15	3.95	2.78	1.6	1.1

TABLE III

TEMPERATURE COEFFICIENT DATA FOR TTA; BEHAVIOR AT 0° C. COMPARED TO 25° C.

Buffer No.	pH	Concn. mM	WAVE I				WAVE II				Type of process	
			$E_a$ v.	$i_d$ ua.	$i_d/c$ ua./mM	Temp. Coeff.	$E_a$ v.	$i_d$ ua.	$i_d/c$ ua./mM	Temp. Coeff.		
2	5.2	0.8	0.953	0.29	0.36	5.5	1.157	2.31	2.89	1.3	Kinetic	Diffusion
			0.983	0.19	0.24	7.0	1.160	2.30	2.87	1.3		
			0.979	0.23	0.29	6.5	1.158	2.26	2.83	1.3		
			0.988	0.15	0.21	7.0	1.160	2.26	2.83	1.3		
			0.987	0.20	0.25	7.0	1.160	2.26	2.83	1.3		
			0.972	0.22	0.30	6-7	1.160	2.26	2.83	1.3		
3	8.2	0.8	1.244	1.91	2.38	4.0	1.389	2.17	2.71	2.5	Kinetic	Diffusion
			1.246	1.87	2.36	4.0	1.391	2.37	2.96	2.0		
			1.250	1.74	2.18	4.0	1.396	2.75	3.45	1.5		
			1.249	1.79	2.24	4.0	1.387	2.39	2.99	2.0		
			1.249	1.77	2.21	4.0	1.387	2.29	2.86	2.3		
4	9.2	0.8	No wave				1.440	3.29	4.12	2.3	Kinetic	Diffusion
			No wave				1.445	3.20	4.00	2.3		
			No wave				1.449	3.28	4.09	2.3		
			No wave				1.447	3.24	4.05	2.3		

TABLE IV

VARIATION OF  $i_d$  OF TTA WITH DROP TIME (MERCURY HEAD) AT 25° C.

Buffer No.	pH	Concn. mM	Height cm.	WAVE I		WAVE II	
				$E_d$ V.	$\frac{i_d}{i_{d65}} \frac{t}{t_{d65}}$ Process	$E_d$ V.	$\frac{i_d}{i_{d65}} \frac{t}{t_{d65}}$ Process
4	9.2	0.8	82	No wave		1.447	6.03 1.12 Diff.
			65	No wave		1.447	5.38
			82	No wave		1.447	5.87 1.09 Diff.
2	5.2	0.8	82	0.991	1.14 1.00 Kinetic	1.163	3.59 1.16 Diff.
			65	0.996	1.14	1.160	3.10
			82	0.995	1.22 1.07 Diff. or Kinetic	1.166	3.59 1.16 Diff.
3	8.2	0.8	82	1.216	4.99 1.06 Diff. or Kinetic	1.399	3.98 1.42 Adsorp.
			65	1.215	4.71	1.389	2.81
			82	1.216	4.83 1.03 Kinetic	1.392	3.85 1.37 Adsorp.

TABLE V  
COMPARATIVE  $E_2$  VALUES FOR TTA AND RELATED COMPOUNDS<sup>a</sup>

Compound	Buffer							
	Chloride		Acetate		Ammonia		Borate	
	$1E_2$	$2E_2$	$1E_2$	$2E_2$	$1E_2$	$2E_2$	$1E_2$	$2E_2$
Thiophene	nw	nw	nw	nw	nw	nw	nw	nw
Trifluoro- acetylacetone	nw	nw	nw	1.22	nw	1.43	nw	nw
Acetothienone	nw	0.96	nw	1.25	nw	1.41	nw	1.47
Thenoylacetone			nw	1.15	1.25	1.45	1.35	1.48
TTA	0.79	0.92	0.98	1.17	1.23	1.39	nw	1.48

<sup>a</sup> nw indicates no wave present while a blank indicates that the compound was not studied in the particular buffer.



TABLE VI  
CLEAVAGE OF TTA IN AMMONIA BUFFER OF pH 8.2

Time, Min.	WAVE I			WAVE II	
	$E_{\frac{1}{2}}$	$i_d$	$k = x/t^a$	$E_{\frac{1}{2}}$	$i_d$
	<u>v.</u>	<u>ua.</u>	<u>ua. min.<sup>-1</sup></u>	<u>v.</u>	<u>ua.</u>
31	1.236	4.45	0.00645	1.411	3.35
31	1.243	4.16	0.00605	1.424	3.22
123	1.235	3.88	0.00602	1.420	3.30
249	1.233	3.15	0.00603	1.415	3.35
323	1.226	2.55	0.00650	1.409	3.51
588	1.219	1.98	0.00454	1.404	3.69
839	1.217	1.22	0.00408	1.400	3.64
1488	1.208	0.65	0.00269	1.395	3.72
1683	1.203	0.60	0.00241	1.388	3.53
1826	1.214	0.34	0.00236	1.388	3.25
2160	No wave			1.383	3.01
2876	No wave			1.382	2.75

<sup>a</sup> The value of  $i_d$  extrapolated to zero time is 4.65 for the first wave.

LEGIBILITY POOR

TABLE VII  
CONSTANCY OF DIFFUSION CURRENT CONSTANT<sup>a</sup> WITH CONCENTRATION

<u>Buffer No.</u>	<u>pH</u>	<u>TTA Concn. mM</u>	<u>First Wave I</u>	<u>Second Wave I</u>	<u>Total Wave I</u>
4	9.2	0.2	nw	5.2	
4	9.2	0.5	nw	5.1	
4	9.2	0.8	nw	5.2	
4	9.2	1.2	nw	4.7	
3	8.2	0.2	4.5	3.0	7.5
3	8.2	0.5	4.3	3.0	7.3
3	8.2	0.8	4.2	3.1	7.3
3	8.2	1.2	4.1	2.9	7.0
2	5.2	0.2	1.0	2.7	3.7
2	5.2	0.5	1.1	2.7	3.8
2	5.2	0.8	1.0	2.8	3.8
2	5.2	1.2	1.1	2.7	3.9

$$^a I = i_d / \text{cm}^2 / 3 t^{1/6}$$

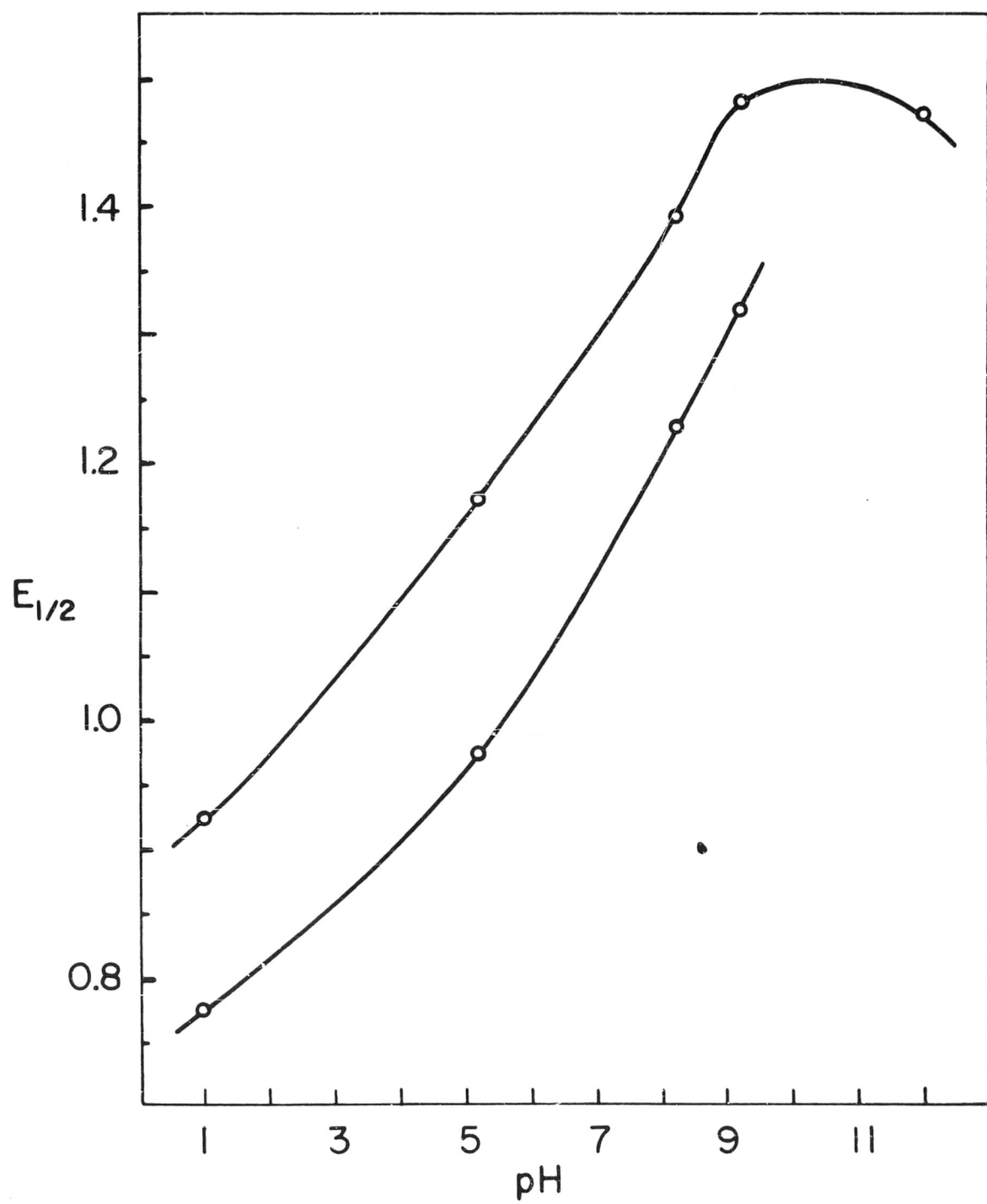
TABLE VIII

POLAROGRAPHIC CONSTANTS OF TTA IN NON-ALCOHOLIC SOLUTIONS AT 25° C. IN ACETATE BUFFER OF PH 5.0

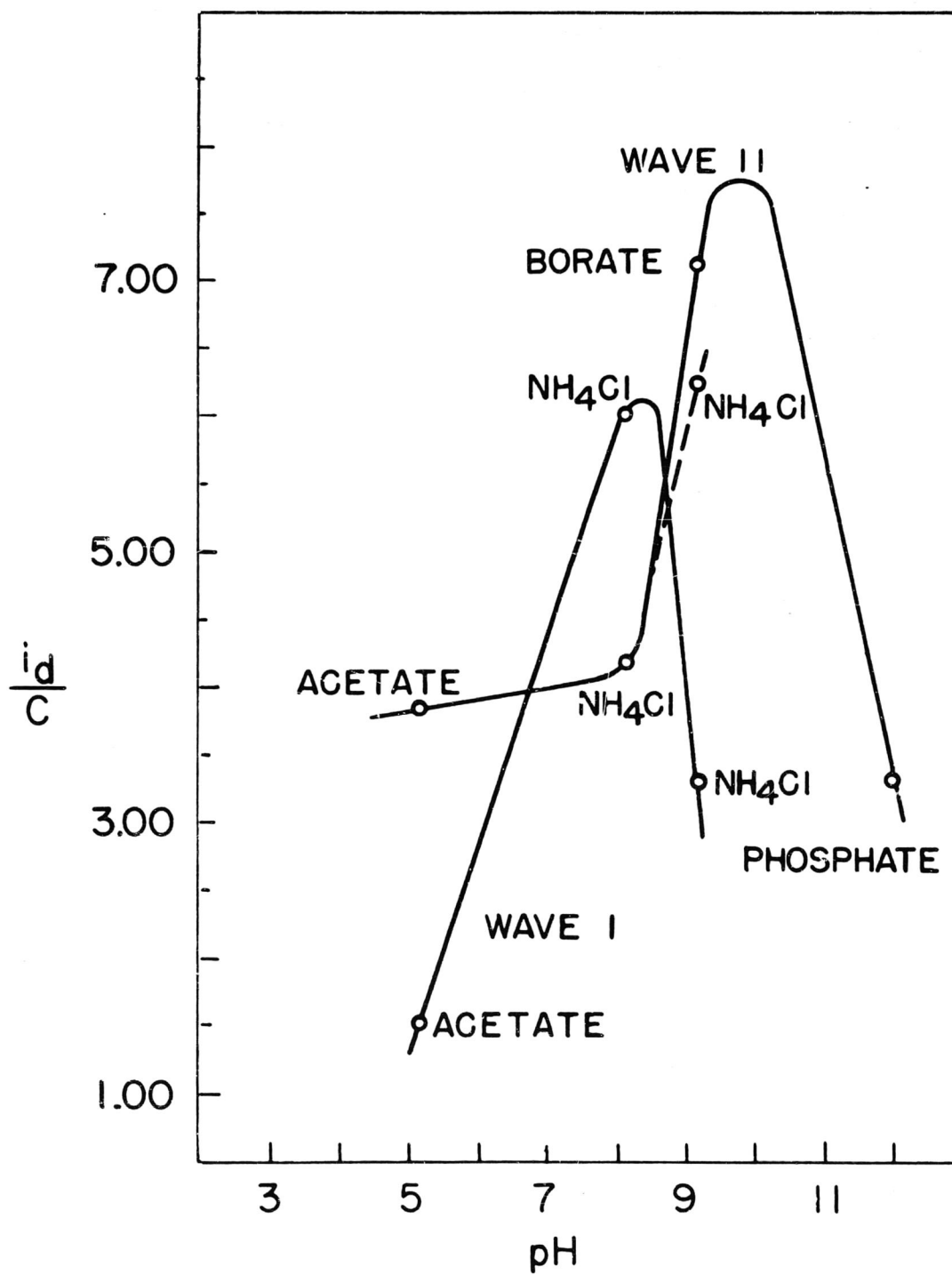
Concn. mM	WAVE I					WAVE II					
	$E_{\frac{1}{2}}$ V.	$i_d^c$ ua.	$i_d/c$ ua./mM	$n^a$	$n^b$	$E_{\frac{1}{2}}$ V.	$i_d^c$ ua.	$i_d/c$ ua./mM	$I_d$	$n^a$	$n^b$
0.1	1.010	0.15	1.52	0.6	2.1	1.172	0.37	3.68	2.59	1.5	1.4
0.1	0.996	0.18	1.78	0.7	1.8	1.158	0.31	3.05	2.12	1.2	2.0
0.2	0.968	0.23	1.14	0.4	1.2	1.160	0.94	4.70	3.33	1.9	1.3
0.2	0.986	0.28	1.40	0.6	1.2	1.157	0.81	4.07	2.86	1.6	1.4
0.3	0.986	0.34	1.14	0.4	1.5	1.160	1.10	3.68	2.59	1.5	1.5
0.3	0.987	0.34	1.14	0.4	1.4	1.158	1.10	3.68	2.59	1.5	1.3
0.5	0.984	0.52	1.04	0.4	1.2	1.156	1.78	3.55	2.50	1.5	1.4
0.5	0.984	0.52	1.04	0.4	1.1	1.156	1.80	3.61	2.54	1.5	1.4
0.5	0.984	0.53	1.07	0.4	1.2	1.156	1.84	3.69	2.60	1.5	1.3
0.5	0.984	0.51	1.04	0.4	1.1	1.157	1.82	3.64	2.56	1.5	1.5
0.5	0.992	0.50	0.99	0.4	1.1	1.158	1.84	3.69	2.60	1.5	1.5
0.5	0.980	0.51	1.02	0.4	1.2	1.159	1.80	3.61	2.54	1.5	1.2
1.0	0.985	0.91	0.91	0.3	1.4	1.160	3.82	3.82	2.69	1.5	1.2
1.0	0.977	1.01	1.01	0.4	1.0	1.158	3.67	3.67	2.58	1.5	1.2
2.0	0.994	1.77	0.89	0.3	1.2	1.162	6.94	3.47	2.44	1.4	1.3
2.0	0.990	1.85	0.92	0.3	1.2	1.163	7.15	3.57	2.51	1.5	1.1

 $\Delta$  Computed from Ilkovic equation. $\nabla$  Computed from mean galvanometer deflection. $\nabla$  Computed from slope of the wave. $\nabla$   $i_d/cm^2/3t^{1/6}$ .

**Fig. 1. Variation of the half-wave potentials of  
the waves of thenoyltrifluoroacetone with pH**



**Fig. 2. Variation of the diffusion current-concentration  
ratio with pH for the waves of 0.5 mM  
thenoyltrifluoroacetone**





**Fig. 3. Variation of diffusion current with concentration.**

A: wave in buffer, pH 9.2. B: combined waves in ammonia buffer, pH 8.2. B-1: wave I in ammonia buffer, pH 8.2. B-2: wave II in ammonia buffer, pH 8.2. C: combined waves in acetate buffer, pH 5.2. C-1: wave I in acetate buffer, pH 5.2. C-2: wave II in acetate buffer, pH 5.2.

